

Novel Polymer Electrolytes Prepared by Copolymerization of Ionic Liquid Monomers

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ABSTRACT

Ionic liquid monomer couples were prepared by the neutralization of 1-vinylimidazole with vinylsulfonic acid or 3-sulfopropyl acrylate. These ionic liquid monomer couples were viscous liquid at room temperature and showed low glass transition temperature (T_g) at -83°C and -73°C , respectively. These monomer couples were copolymerized to prepare ion conductive polymer matrix. Thus prepared ionic liquid copolymers had no carrier ions, and they showed very low ionic conductivity of below $10^{-9} \text{ S cm}^{-1}$. Equimolar amount of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) to imidazolium salt unit was then added to generate carrier ions in the ionic liquid copolymers. Poly(vinylimidazolium-co-vinylsulfonate) containing equimolar LiTFSI showed the ionic conductivity of $4 \times 10^{-8} \text{ S cm}^{-1}$ at 30°C . Advanced copolymer, poly(vinylimidazolium-co-3-sulfopropyl acrylate) which has flexible spacer between the anionic charge and polymer main chain, showed the ionic conductivity of about $10^{-6} \text{ S cm}^{-1}$ at 30°C , which is 100 times higher than that of copolymer without spacer. Even an excess amount of LiTFSI was added, the ionic conductivity of the copolymer kept this conductivity. This tendency is completely different from the typical polyether systems. Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: Ionic liquid; Molten salt; Ionic conductivity; Glass transition temperature; Solid polymer electrolyte

INTRODUCTION

Recently, air- and water-stable ionic liquids have been prepared by the combination of imidazolium cation and specific organic anions [1, 2]. Since these ionic liquids are composed of only ions, they have very high carrier ion concentration and accordingly show high ionic conductivity at room temperature [3–7]. Furthermore, ionic liquids are widely spread as some kinds of reaction media and extraction solvent, because of very unique properties, such as nonvolatility, low viscosity, and immiscible with water when fluorine-rich anions were used [8–11].

Since ionic liquids are empirically known to be prepared with imidazolium salts, several imidazolium cation derivatives are used to form ionic liquids [12]. The ionic liquids are generally prepared through the anion exchange process from salts having halide anions. There are some drawbacks such as incomplete anion exchange process and contamination of by-products. In addition, this method is limited for only several anion species. Development of new ionic liquids is not so rapid, in spite of unlimited combination of cations and anions [1–7].

We then proposed novel synthesis method to prepare ionic liquid by the neutralization of the tertiary amines with acids [13, 14]. This method is

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useful for not only the improvement of the synthesis but also the analysis of the relation between ionic liquid structure and their properties (glass transition temperature, melting point, viscosity, ionic conductivity, and so on). This neutralization method is capable to prepare desired ionic liquid from one pot reaction without any by-product. We discussed the effect of counter anions on the properties of ionic liquid by changing acid species [14]. Ionic liquids thus prepared by the neutralization method are suitable as model compounds for dialkylimidazolium salts. Several important factors of amines and acids were obtained to design excellent ionic liquids.

Since ionic liquids show excellent ionic conductivity, they are also investigated as a component of an electrolyte matrix. Especially, the developments of polymer gel electrolytes have been carried out with polymers containing ionic liquids [15-17]. However, ordinary ionic liquids are improper as an electrolyte, because component ions of ionic liquid migrate along with the potential gradient. This is a fatal drawback when only target ions such as lithium cations are aimed to be transported.

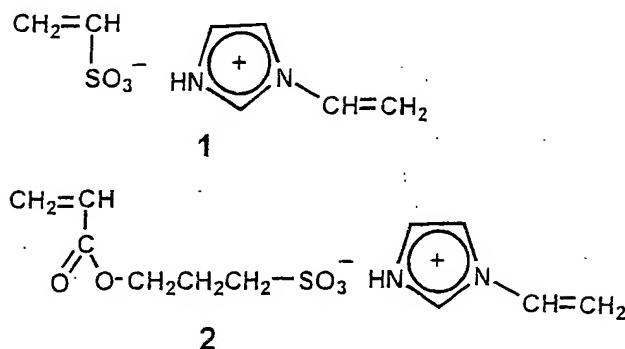
We have reported two methods to solve such a problem. One is the zwitterionic-type ionic liquid, of which both cation and counter anion were tethered [18]. The other is the ionic liquid polymer, in which cations or counter anions were attached on the vinyl polymer [19]. Although zwitterionic-type ionic liquids have relatively high T_m , lithium transference numbers in these zwitterionic-type ionic liquids exceed 0.5. Such a matrix should be suitable for target ion transport when the ion migration was accelerated. On the other hand, we have designed ionic liquid polymers such as polycation [20, 21], polycation-type polymer brush [22, 23], and polyanion [24, 25]. These are obtained by the polymerization of ionic liquid monomers, which have vinyl groups on either cations or counter anions. In addition, polymerization of ionic liquid is effective to not only transport target ions selectively but also generate carrier ions. It is widely known that cationic and anionic polymers offer an atmosphere with high dielectric constant, which facilitates the dissociation of lithium salts in the matrix [26]. However, polymerization of ionic liquid components induced considerable decrease in the mobility of ions in the matrix due to the increase of glass transition temperature. So far, it is necessary to increase mobility of ionic liquid structure by introducing spacer between polymer main chain and salt structure [22, 23].

In this paper, we introduced vinyl groups in both cation and anion, and novel ionic liquid polymers were prepared by the copolymerization of these ionic liquid monomers.

EXPERIMENTAL

Materials

1-Vinylimidazole and 3-sulfopropyl acrylate potassium salt were purchased from Aldrich Chemical



SCHEME 1. Structure of ionic liquid monomers obtained by neutralization.

Co. Sodium vinylsulfonate was purchased from Kanto Chemical Co. Inc. These were used as received. α, α' -Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol before use.

Lithium bis(trifluoromethanesulfonyl)imide (Li TESI) was a gift from Sumitomo 3M corporation.

Synthesis of ionic liquid monomers

Alkali metal cations of sodium vinylsulfonate and 3-sulfopropyl acrylate potassium salt were substituted into proton by means of cation exchange resin (Amberlite IR-120B H AG). Aqueous solutions of these acids were slowly mixed with equimolar amount of 1-vinylimidazole on ice bath. The mixture was stirred at room temperature for a day. The aqueous solution was then dried with a rotary evaporator; the residual viscous liquid was poured into dehydrated diethyl ether and stirred for 1 hour. The viscous liquid was collected and dried. This was repeated twice and the obtained salt was dried *in vacuo* at room temperature. The structure of the obtained ionic liquid monomers as shown in Scheme 1 was confirmed with $^1\text{H-NMR}$.

Polymerization of ionic liquid monomers

Radical polymerization of these monomers was initiated with AIBN (1 mol%) in ethanol at 60°C under N_2 atmosphere. After polymerization, the solution was poured into a large excess acetone. Precipitation was washed with dehydrated methanol and dried *in vacuo* at 60°C.

Methods

The structure of these ionic liquid monomers was confirmed by $^1\text{H-NMR}$ spectroscopy (JEOL α -500 NMR spectrometer).

The ionic conductivity of the obtained compounds was measured with the complex-impedance method using an impedance analyzer (Schlumberger Solartron 1260 impedance/gain-phase analyzer) with a frequency range from 10 Hz to 5 MHz. The dynamic ionic conductivity measurement system was developed in our laboratory [27]. All measurements were carried out in a

TABLE 1. Effect of polymerization time on the ionic conductivity and T_g

	Polymerization Time (h)	T_g ($^{\circ}\text{C}$)	σ_i at 30°C (S cm^{-1})	State
1	Monomer	-83	3.5×10^{-3}	Liquid
P1a	3	-75	8.5×10^{-5}	Rubber-like
P1b	6	—	$< 10^{-9}$	Solid
P1c	12	—	$< 10^{-9}$	Solid
P1	24	—	$< 10^{-9}$	Solid

—; not detected

globe box under dry N_2 atmosphere in the temperature range 10°C to 60°C at a cooling rate of $2.5^{\circ}\text{C min}^{-1}$.

DSC measurement was carried out with a DSC-6200 (Seiko Instruments Inc.) in the temperature range -150°C to 200°C at a heating rate of $10^{\circ}\text{C min}^{-1}$.

RESULTS AND DISCUSSION

Ionic liquid monomer **1** was obtained as a yellow transparent viscous liquid at room temperature. It is known that imidazolium salts with fluorinated anions, like BF_4^- , CF_3SO_3^- , and TFSI^- , form excellent ionic liquid [6]. The monomer **1** was obtained as liquid with T_g of -83°C . Viscosity of **1**, however, exceeds 1000 cP at room temperature, which is much higher than that for other typical ionic liquids. In spite of high viscosity, **1** showed relatively high ionic conductivity of $3.5 \times 10^{-3} \text{ S cm}^{-1}$ at room temperature reflecting low T_g .

Ionic liquid copolymer P1 (P implies polymer) has been prepared by copolymerization of ionic liquid monomer **1**. Table 1 summarizes the effect of polymerization time on the ionic conductivity and T_g for **1**. When polymerization time was 3 hours, rubber-like polymer P1a with T_g of -75°C was obtained. Only when the polymerization time exceeded 6 hours, polymerized **1** became solid or powder. An obvious T_g for these polymers cannot be detected with DSC apparatus used in our experiments.

Since the copolymers have no carrier ions because both cations and anions were fixed on polymer main chain, they should show very poor ionic conductivity. P1a showed relatively high ionic conductivity of $8.5 \times 10^{-5} \text{ S cm}^{-1}$ at 30°C . This can be comprehended to be due to low molecular weight matrix, like oligomer. On the other hand, the ionic conductivity of P1b, P1c, and P1, which were prepared by longer polymerization time (> 6 hours), was less than $10^{-9} \text{ S cm}^{-1}$ at 30°C . Although the molecular weight of P1 was not measured yet, improved average molecular weight was confirmed as the decrease of the ionic conductivity. Unless otherwise stated, polymerization time of P1 is 24 hours hereafter.

In order to characterize P1 as an ion conductive matrix, three kinds of lithium salts (LiBF_4 , LiCF_3SO_3 , and LiTFSI) were added equimolarly to imidazolium salt unit of P1. Fig. 1 shows temperature dependence of the ionic conductivity for P1 containing equimolar amount of lithium salt. P1 with LiTFSI showed ionic conductivity of $7.2 \times 10^{-7} \text{ S cm}^{-1}$ at 50°C , whereas that of P1 with LiCF_3SO_3 or LiBF_4 was only $10^{-9} \text{ S cm}^{-1}$. This considerable increase in the ionic conductivity by the addition of LiTFSI cannot be explained only by higher degree of dissociation of the added salt. TFSI^- is known to act as a plasticizer [28], and this was also confirmed in the case of this copolymer. However DSC measurements were performed for these samples, their T_g was not detected clearly. The lowering of T_g cannot be confirmed with the DSC measurement, but the increase of the ionic

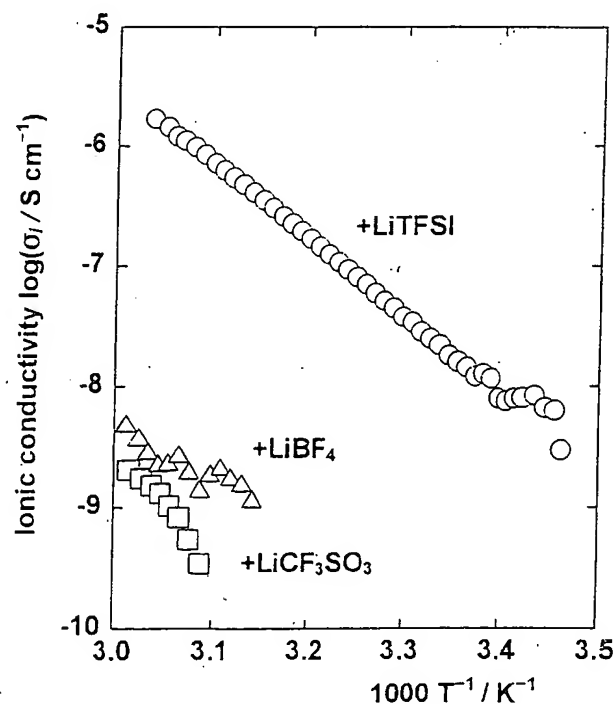


FIGURE 1. Temperature dependence of the ionic conductivity for P1 containing LiX ($\text{X} = \text{BF}_4^-$, CF_3SO_3^- , TFSI^-). $[\text{LiX}]/[\text{Im}^+] = 1.0$ (by mol ratio)

TABLE 2. The ionic conductivity at room temperature and T_g of each monomers and their copolymers

	T_g ($^{\circ}\text{C}$)		σ_i (S cm^{-1})	
	Monomer	Polymer	Monomer	Polymer
<u>1</u>	-83	—	3.5×10^{-3}	$< 10^{-9}$
<u>2</u>	-73	-31	6.5×10^{-4}	$< 10^{-9}$

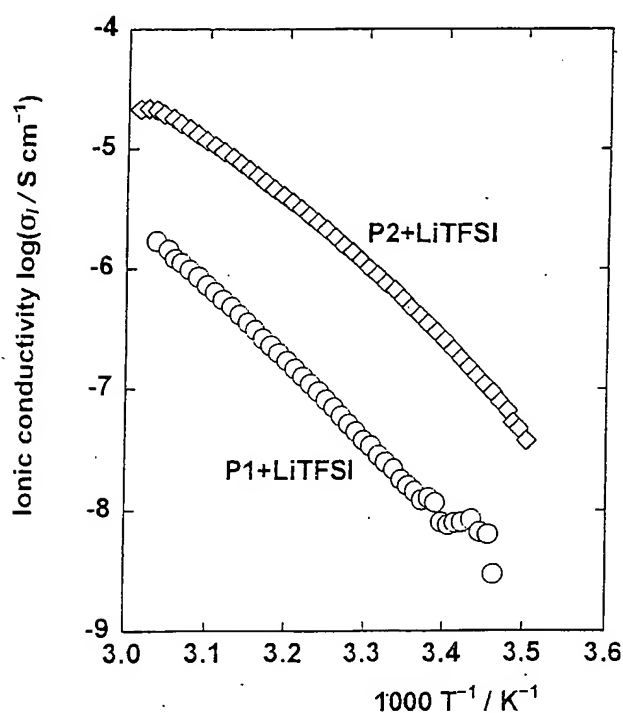
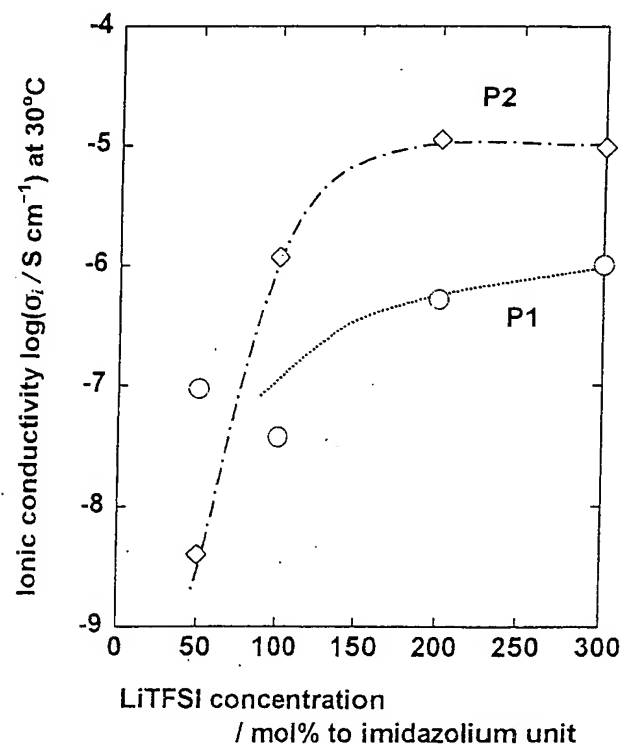
—; not detected
 Polymers were obtained by the copolymerization of corresponding monomers for 24 hours.

conductivity clearly indicated it. Similar tendency was reported on the zwitterionic-type ionic liquids [18].

However P1, mixed with equimolar amount of LiTFSI, showed the highest ionic conductivity among three, this needs further improvement on the ionic conductivity. For this, we designed new ionic liquid copolymer, which have flexible spacer between vinyl group and counter anion structure expecting higher segmental motion. In our previous study, comb-shaped polymers were analyzed, and introduction of spacer between polymer main chain and cation charge was revealed to be effective to maintain high ionic conductivity even after polymerization [22, 23]. Table 2 shows T_g and the ionic conductivity of ionic liquid monomers 1, 2, and corresponding their copolymers. Compound 2 is liquid at room temperature as well as 1 and

shows the T_g at -73°C . In spite of low T_g , the ionic conductivity of 2 was $6.5 \times 10^{-4} \text{ S cm}^{-1}$ at room temperature, which is one order lower than that of 1. We considered that larger anion structure of ionic liquid monomer 2 leads to lower ionic conductivity. After polymerization for 24 hours, P2 showed very low ionic conductivity (less than $10^{-9} \text{ S cm}^{-1}$) similarly to that of P1. P1 showed no T_g at the temperature range for this measurement, whereas P2 showed relatively low T_g of -31°C . From these, P2 containing lithium salt was expected to show higher ionic conductivity than that of P1.

Equimolar amount of LiTFSI was also added to P2 to compare the ionic conductivity. P2 containing equimolar LiTFSI showed the ionic conductivity of $1.2 \times 10^{-6} \text{ S cm}^{-1}$ at 30°C , which was 30 times higher than that of P1 as shown in Fig. 2. This difference is attributed to the following two factors:

**FIGURE 2.** Temperature dependence of the ionic conductivity for P1 and P2 containing LiTFSI. $[\text{LiTFSI}] /$ **FIGURE 3.** Effect of LiTFSI concentration on the ionic conductivity for P1 and P2

one is the increase of free volume by the introduction of spacer group, and the other is the improvement of flexibility of ionic liquid moiety by the alkyl spacer. The introduction of spacer was effective to maintain the segmental motion high. The polymer systems having spacers onto cation site or both sites are now in progress.

The effect of LiTFSI concentration on the ionic conductivity of P1 or P2 was investigated. The ionic conductivity increased with increasing the amount of LiTFSI for both P1 and P2 as shown in Fig. 3. The ionic liquid copolymers containing excess LiTFSI (200 ~ 300 mol%) showed a constant ionic conductivity. The ionic conductivity of P2 is 10 ~ 20 times higher than that of P1. As mentioned above, this difference was based on the introduction of alkyl spacer. P2 maintains relatively high ionic conductivity at even high salt concentration. It is well known that the ionic conductivity of polyether systems was lowered by the addition of only small excess of salts. In poly(ethylene oxide) systems, the ionic conductivity decreased by the addition of small excess salts due to the elevation of T_g . We therefore attempted to discuss the different salt concentration dependence by means of T_g , however their T_g could not be determined with DSC measurement. This problem may be based on the distribution of molecular weight for these ionic liquid polymers. Continuous study has been carried out and results will be reported soon. It is possible to obtain more excellent ionic liquid polymers with higher ionic conductivity by the suitable molecular design of starting ionic liquid monomers.

CONCLUSION

We obtained novel ionic liquid copolymers prepared by the radical polymerization of 1-vinylimidazole neutralized with acids having vinyl group. Ionic liquid copolymer showed very low ionic conductivity of below 10^{-9} S cm $^{-1}$ at 50°C. When equimolar amount of LiTFSI was added, poly-(vinylimidazolium-co-vinylsulfonate) showed the ionic conductivity of 7.2×10^{-7} S cm $^{-1}$ at 50°C. On the other hand, ionic liquid polymer having flexible spacer showed the ionic conductivity of 1.2×10^{-5} S cm $^{-1}$ at 50°C, which was about 20 times higher than that for polymer without spacer. It was revealed that flexible spacer is effective to improve the ionic conductivity of ionic liquid polymers after addition of salt.

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REFERENCES

1. Wilkes JS, Zaworotko MJ. Air and Water Stable 1-Ethyl-3-methylimidazolium Based Ionic Liquids. *J. Chem. Soc., Chem. Commun.* 1992; 965.
2. Fuller J, Carlin RT, De Long HC, Haworth D. Structure of 1-Ethyl-3-methylimidazolium Hexafluorophosphate: Model for Room Temperature Molten Salts. *J. Chem. Soc. Chem., Commun.* 1994; 299.
3. Koch VR, Nanjundiah C, Appetecchi GB, Scrosati B. The Interfacial Stability of Li with Two New Solvent-Free Ionic Liquids: 1,2-Dimethyl-3-propylimidazolium Imide and Methide. *J. Electrochem. Soc.* 1995; 142: L116.
4. Bonhôte P, Dias A, Armand M, Papageorgiou N, Kalyanasundaram K, Grätzel M. Hydrophobic, Highly Conductive Ambient-Temperature Molten Salts. *Inorg. Chem.* 1996; 35: 1168.
5. Hagiwara R, Hirashige T, Tsuda T, Ito Y. Acidic 1-Ethyl-3-methylimidazolium Fluoride: A New Room Temperature Ionic Liquid. *J. Fluorine Chem.* 1999; 99: 1.
6. (a) MacFarlane DR, Meakin P, Sun J, Amini N, Forsyth M. Pyrrolidinium Imides: A New Family of Molten Salts and Conductive Plastic Crystal Phases. *J. Phys. Chem. B* 1999; 103: 4164. (b) MacFarlane DR, Huang J, Forsyth M. Lithium-Doped Plastic Crystal Electrolytes Exhibiting Fast Ion Conduction for Secondary Batteries. *Nature* 1999; 402: 792.
7. McEwen AB, Ngo HL, LeCompte K, Goldman JL. Electrochemical Properties of Imidazolium Salt Electrolytes for Electrochemical Capacitor Applications. *J. Electrochem. Soc.* 1999; 146: 1687.
8. Seddon KR. Ionic Liquids for Clean Technology. *J. Chem. Tech. Biotechnol.* 1997; 68: 351.
9. Welton T. Room-Temperature Ionic Liquids. Solvents for Synthesis and Catalysis. *Chem. Rev.* 1999; 99: 2071.
10. Itoh T, Akasaka E, Kudo K, Shirakami S. Lipase-Catalyzed Enantioselective Acylation in the Ionic Liquid Solvent System: Reaction of Enzyme Anchored to the Solvent. *Chem. Lett.* 2001; 262.
11. Huddleston JG, Willauer HD, Swatoski RP, Visser AE, Rogers RD. Room Temperature Ionic Liquids as Novel Media for 'Clean' Liquid-Liquid Extraction. *Chem. Commun.* 1998; 1765.
12. Wilkes JS, Levisky JA, Wilson RA, Hussey CL. Dialkylimidazolium Chloroaluminate Melts: A New Class of Room-Temperature Ionic Liquids for Electrochemistry, Spectroscopy, and Synthesis. *Inorg. Chem.* 1982; 21: 1263.
13. Hirao M, Sugimoto H, Ohno H. Preparation of Novel Room-Temperature Molten Salts by Neutralization of Amines. *J. Electrochem. Soc.* 2000; 147: 4168.
14. Yoshizawa M, Ogihara W, Ohno H. Design of New Ionic Liquid by Neutralization of Imidazole Derivatives with Imide-Type Acids. *Electrochem. Solid-State Lett.* 2001; 4: E25.
15. Fuller J, Breda AC, Carlin RT. Ionic Liquid-Polymer Gel Electrolytes form Hydrophilic and Hydrophobic Ionic Liquids. *J. Electroanal. Chem.* 1998; 459: 29.
16. Carlin RT, De Long HC, Fuller J, Trulore PC. Dual Intercalating Molten Electrolyte Batteries. *J. Electrochem. Soc.* 1994; 141: L73.
17. Noda A, Watanabe M. Highly Conductive Polymer Electrolytes Prepared by in situ Polymerization of Vinyl Monomers in Room Temperature Molten Salts. *Electrochim. Acta* 2000; 45: 1265.
18. Yoshizawa M, Hirao M, Ito-Akita K, Ohno H. Ion

- Conduction in Zwitterionic-Type Molten Salts and Their Polymers. *J. Mater. Chem.* 2001; 11: 1057.
19. Ohno H. Molten Salt Type Polymer Electrolyte. *Electrochim. Acta* 2001; 46: 1407.
 20. Hirao M, Ito K, Ohno H. Preparation and Polymerization of New Organic Molten Salts; N-alkylimidazolium salt derivatives. *Electrochim. Acta* 2000; 45: 1291.
 21. Hirao M, Ito K, Ohno H. Polymerization of Molten Salt Monomers Having a Phenylimidazolium Group. *Polym. Adv. Technol.* 2000; 11: 534.
 22. Yoshizawa M, Ohno H. Molecular Brush Having Molten Salt Domain for Fast Ion Conduction. *Chem. Lett.* 1999; 889.
 23. Yoshizawa M, Ohno H. Synthesis of Molten Salt-Type Polymer Brush and Effect of Brush Structure on the Ionic Conductivity. *Electrochim. Acta* 2001; 46: 1723.
 24. Ohno H, Ito K. Room-Temperature Molten Salt Polymers as a Matrix for Fast Ion Conduction. *Chem. Lett.* 1998; 751.
 25. Yoshizawa M, Ogihara W, Ohno H. Preparation and Ionic conductivity of Molten Salt-Type Anionic Polymers. *Polymer Preprints, Japan* 2000; 49: 3213.
 26. Takeoka S, Maeda Y, Kitahara Y, Tsuchida E. Ion Dissociation of Salts in Polyion Complexes and Adding Effect of Poly(oxyethylene). *Polymer Preprints, Japan* 1991; 40: 594.
 27. Ohno H, Inoue Y, Wang P. Temperature-Controlled Ionic Conductivity Switching in Poly [oligo(oxyethylene) methacrylate]/Poly(ethylene oxide) layered Film. *Solid State Ionics* 1993; 62: 257.
 28. Besner S, Vallee A, Bouchard G, Prud'homme J. Effect of Anion Polarization on Conductivity Behavior of Poly(ethylene oxide) Complexed with Alkali Salts. *Macromolecules* 1992; 25: 6480.